Dear Editor, Dear Referee,

We would like to thank you very much for your positive feedbacks and detailed suggestions to improve our revised manuscript.

We reply to these comments individually below and will also address them where possible in the newly revised version (marked-up version, line numbers mentioned below refer to this version). Reviewer comments are reproduced in **bold**, with our explanations in *italic*. We also listed the further changes regarding to language improvements at the end.

Wenkui He

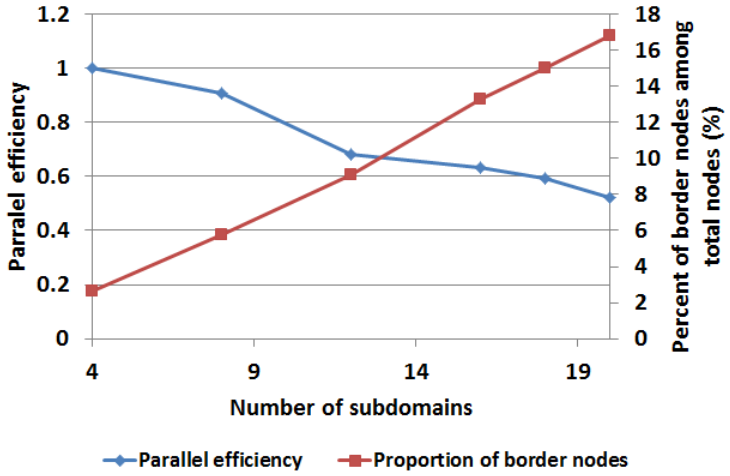
On behalf of all authors

Response to Glenn Hammond

1	**Thank you for your responses to the previous questions. I am satisfied with the responses. I apologize for the additional questions below, but there is so much new content in the revised paper that I have additional questions/concerns.**
	Thank you very much for your positive feedback and careful review. We improved our manuscript further based on your comments. We address these comments individually below.
2	**The grammar in the paper is awkward in many locations. I highly recommend that a native English speaker edit/revise some of the wording. Several situations are listed below, but there are many more. This should not be too difficult.**
	Thank you for improving the language. Besides correcting the sentences mentioned by you, we revised the whole manuscript with the help of a native English speaker. These changes are listed at the end.
3	**(Page) 2: Line 4-5: "…and more straightforwardly on high performance computers" – needs to be revised as this does not make sense. Easier?**
	We changed "more straightforwardly" as "easier" (2: Line 4).
4	**2: Line 10: "almost any chemical reaction"? How about "many chemical reactions" or "numerous chemical reactions"?**
	Thank you, we think "numerous chemical reactions" is better (2: Line 7).
5	**3:Line 8: "coupling of different codes…is an indispensable choice" – this is solely opinion.**
	We deleted "an indispensable choice and" (3: Line 10).
6	**4: Line 7: Since Hammond et al., 2012 is cited but not included in the references, you may want to review all citations to ensure that the references exist at the end.**
	Thank you very much for the careful check. We apologize for our careless mistakes. We added the reference for this citation, and checked all the other citations and references. *We corrected the citation "Kosakowski and Watanabe, 2013" as "Kosakowski and Watanabe, 2014" in 2:Line 25; 3: Line 15, 24 and 6: Line 22. We corrected the reference in 27: Line 4.*
7	**5:Line 4: "therefore a speedup for flow/transport is not given anymore". Should this be "is not experienced anymore".**
	We changed "not given anymore, if…" as "no longer experienced when …" (5: Line 7).
8	**5:Line 12: "flexible distribution of different amount of computer resources" -> amounts?**

	We corrected "amount" as "amounts" (5: Line 18).
9	**6:Line 25: "It provides a well-defined series of methods" How about "it provides an API (Application Programming Interface)".**
	Thank you for the nice suggestion, we changed the sentence as "it provides an application programming interface (API)" (7: Line 7).
10	**7: Line 18: The reference to CMake is out of the blue. How about calling it the build system? Otherwise, you need to explain CMake.**
	We changed "the CMake file" as "the build system" (8: Line 1).
11	**9: Line 19: Lasaga type rate law -> it is referred to as "transition state theory" (and then cite Lasaga)**
	Thanks, we adopted your suggestion (10: Line 3).
12	**10: Line 5: "IPhreeqc interface and the overhead involved in calling IPhreeqc are 12.7% and 3.8%". Can you point me to where you explain/define the difference between the interface and overhead? I assume that the initialization of the thermodynamic database is in the overhead….**
	In Sect. 2.3 (9: Line 11) we defined the compositions of the overhead involved in calling IPhreeqc. Yes, the loading of the thermodynamic database is included in the overhead. To make it clearer to the reader, we added • *explanation of the time consumption for the interface as "(including the preparation of input for IPhreeqc and the processing of output from IPhreeqc)", after "IPhreeqc interface" (10: Line 18);* • *"(described in Sect. 2.3)" after "the overhead involved in calling IPhreeqc" (10: Line 19).*
13	**11: Line 12: The description of domain decomposition leads me to believe that you are using Richardson iteration (i.e. where one solves the local subdomain and then updates the ghost/halo values), but I find that hard to believe. With domain decomposition, the linear/nonlinear system is solved across the entire domain for each iteration. If you are truly iterating between subdomains, I highly recommend using the full implicit solve as it would converge much faster. 11: Line 24: Again, this doesn't sound like traditional domain decomposition.**
	We are using the domain decomposition for partitioning the computing tasks of • *assembly of subdomain matrices and vectors* • *solving global equation system parallel with iterative Krylov subspace equation solver* *With the current approach, the stiffness matrices and vectors are assembled within subdomains, and the Krylov subspace solver collects the norms of the production of the subdomain matrices and vectors to compute a converged solution.* *More details of the DDC approach can be found in Wang et al. (2009).* *To avoid misunderstanding we renamed the section title as "Application of the DDC approach of OGS" and rewrote the whole part as:* *"The domain decomposition approach (DDC) is applied to partition the computational tasks of the global assembly and the linear solver implemented in OGS (Wang et al, 2009).* *For the current DDC approach, METIS is used as a preprocessing tool to partition mesh in order to balance the node quantities and minimize the border nodes among subdomains efficiently. With the partitioned mesh data, the stiffness matrix and the right-hand side vector of the system of linear equations are only assembled within subdomains by individual compute cores. Then these assembled subdomain matrices and vectors are taken to compute a converged solution with iterative solvers. By this way, the computational tasks of the global assembly and the linear solver are parallelized straightforwardly."*
14	**12: Line 21: "a single input string will be prepared" – is there a separate string for each cell (all concentrations in each cell) or is there a single string for all concentrations in all cells being**

	solved on a core?
	In a serial simulation, only one input string will be prepared for all nodes (cells) during each time step. In a parallel simulation, one input string will carry the concentration values for the nodes being solved on a specific compute core. We modified the sentence "a single input string will be prepared" as "only one input string will be prepared for all finite element nodes" (13: Line 15). *We rewrote the sentence ", whose number is equal … employed." as ". Each string carries the information for the nodes being solved on a specific compute core." (13: Line 18).*
15	**13: Line 11: Are the concentrations in the strings full (double) precision?**
	For the presented simulations, the output string is set to scientific notation with precision 12. We changed this in the meanwhile to 16.
16	**13: Line 28: An MPI_Allreduce() creates a copy of the full buffer for each process. So, you are generating a full global concentration vector for each core? Are you sure that this is not a gather or scatter operation? That seems more reasonable.**
	Yes, we used MPI_Allreduce(). The reviewer is right that it will generate a full global concentration vector for each core. In the current implementation, the grouping of the nodes for solving geochemical reactions is independent of DDC (described in 14: Line 13). We use MPI_Allreduce() as a straightforward solution to collect concentrations from different local buffers and then return the concentrations back to different cores for the following calculation of mass transport. In this way, we do not need to consider the complex tracking of indices when updating concentration values in different cores. *Nevertheless, we are aware that more sophisticated ways should be developed to minimize the memory usage and communication among different cores. We are grateful for the suggestions of the reviewer and will try to use gather or scatter operation to improve our code.* *In the manuscript, we added the following text after "MPI_Allreduce method" (14: Line 24):* *"(it's a straightforward solution for the current implementation. A more sophisticated approach, however, should be implemented to minimize the inter-processor communication and memory usage)"*
17	**15: Line 21: To me it seems that from Figure 8b, the best (fastest) combination would be 18 subdomains (best flow and transport speedup) + 20 geochemistry cores (best chemistry speedup). Just a comment.**
	Thank you for the careful observation, that's right. In 16: Line 25, we changed "when the number of compute cores exceeds 16" into "when 18 DDCs are applied".
18	**15: Line 28: My experience is that parallel efficiency can degrade significantly well before the number of border (ghost) nodes approaches the total number of nodes.**
	In response to this comment, we evaluated the parallel efficiency (for flow and transport) and the number of border nodes for different DDCs for this 2D example. Based on the results we obtained (see the figure below), we think the reviewer is right and modified the whole sentence as follows (16: Line 27): *"In this example, the parallel efficiency for solving flow and mass transport degrades already when more than 8 DDCs are employed, for which the border nodes only account for around 6% of the total nodes. Further increase of the number of DDCs up to 20, yielding 17% of border nodes, decreases the parallel efficiency down to 0.5 almost linearly."*

	
19	**16: Line 14: Averagely -> On average?**
	Yes, it should be "On average," (17: Line 19).
20	**16: Line 16: Let the reader come to this conclusion on their own as some may disagree.**
	We removed the whole sentence (17: Line 21).
21	**18: Line 9: The addition of the uranium leaching problem, an example that clearly illustrates the benefit of this algorithm, greatly improves the paper.**
	Thank you for the comment.
22	**20: Line 14: I believe that where this new algorithm will pay off is with massively parallel computation (hundreds of thousands of cores) where linear solver performance is poor. In those cases, one would want to use fewer cores to solve flow and transport, as conventional parallel preconditioners tend to degrade in performance at extremely large core counts.**
	Thank you for the comment. Due to the limited computational resources available (maximum 300 cores for each user) we could not test our approach for massively parallel computation in the present study. Nevertheless, your argument is a strong encouragement for our future researches and developments, when more computational resources become available. We added the following sentence in order to be more precise (21: Line 17): *"and a continuous speedup can be obtained (with the compute cores that are available) for the calculation of flow and mass transport," before "then using the conventional DDC approach …"*

Additional changes

Positions	*Changes*
5: Line 1	*"optimum amount" -> "optimum amounts"*
5: Line 15	*"reactions system" -> "reaction system"*
3: Line 9; 5: Line 21; 6: Line 17; 11: Line 9; 13: Line 4; 16: Line 12, 19, 27; 19:Line 29; 20:Line 22	*add the article "the"*
3: Line 10	*"applies" -> "applied to"*
3: Line 22	*remove the ","*

3: Line 26	*remove "scales"*
4: Line 27	*remove "additionally"*
4: Line 28	*"…open source, i.e." => "…open source; thus," "could" => "can"*
5: Line 5	*"is" => "are", "so" => "meaning"*
5: Line 8	*"an efficient … more compute cores." => "whereas the computation of the chemical system can see a further speedup with the addition of more compute cores, the computation of the transport problem may already reach a point of optimization, rendering the addition of further compute cores beyond this point inefficient."*
5: Line 14; 6: Line 13	*"applied for" => "applied to"*
5: Line 25	*remove "in the following"*
5: Line 28	*"apply … on" => "apply … to"*
6: Line 10	*"different kind of" => "different kinds of"*
6: Line 12	*"two phase" => "two-phase"*
6: Line 20	*"kinetically controlled biogeochemical-reactions" => "kinetically-controlled biogeochemical reactions"*
7: Line 3	*"widely used" => "widely-used"*
7: Line 5	*"Beside" => "Besides"*
9: Line 11	*"calling of functions" => "steps"*
9: Line 27	*"describes" => "shows"*
10: Line 4	*remove "the" before "dolomite"*
10: Line 13	*"Dolomite" => "dolomite"*
10: Line 30, 19: Line 17	*"Totally" => "In total"*
11: Line 13	*Remove "as much as"*
12: Line 24	*"decomposition procedure" -> "DDC procedure"*
14: Line 3	*"As a special case" => "In special cases"*
14: Line 14	*"independent from" => "independent of"*
15: Line 13	*"Of course jobs…" => "Jobs…"*
16: Line 2	*"differ with" => "differ from"*
17: Line 8	*", hence …" => "; hence,"*
17: Line 12	*add "," after "With a DDC=4"*
17: Line 18	*add "and" before "handing output…"*
18: Line 9	*"lower number of" => "fewer"*
18: Line 12	*add "this" after "The reason behind"*
18: Line 15	*"comparing" => "compared"*
18: Line 25	*"big" => "significant"*
19: Line 8	*"more close" => "closer"*
19: Line 21	*"A total …" => "The total…"*
19: Line 28	*"Best speedups" => "The best speedups"*
19: Line 25	*"between 8 to 16" => "between 8 and 16"*
20: Line 12	*"…coupling, when…"=> "…coupling when a"*
20: Line 13	*"in-" => "input-"*
21: Line 8	*"Particularly" => "In particular"*
21: Line 13	*"compute resources" => "computational resources"*
21: Line 21	*"become" => "becomes"*
21: Line 22	*"middle sized" => "middle-sized", "system" => "systems"*

21: Line 24	*“when further increase” => “when a further increase”*
22: Line 3	*“for large number of” => “for a large number of”*
22: Line 9	*add “in” after “involved”*
22: Line 14	*“remain as” => “remain”*
22: Line 15	*“resource was” => “resources were”*
23: Line 8	*“supports” => “support”*
23: Line 9	*“helps” => “help”*

Manuscript prepared for Geosci. Model Dev. Discuss.
with version 2015/04/24 7.83 Copernicus papers of the LaTeX class copernicus.cls.
Date: 25 September 2015

A parallelization scheme to simulate reactive transport in the subsurface environment with OGS#IPhreeqc 5.5.7-3.1.2

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Abstract

The open source scientific software packages OpenGeoSys and IPhreeqc have been coupled to setup and simulate thermo-hydro-mechanical-chemical coupled processes with simultaneous consideration of aqueous geochemical reactions faster and ~~more straightforwardly~~ easier on high performance computers. In combination with the elaborated and extendable chemical data base of IPhreeqc, it will be possible to setup a wide range of multi-physics problems with ~~almost any chemical reaction~~ numerous chemical reactions that is known to influence water quality in porous and fractured media. A flexible parallelization scheme using MPI (Message Passing Interface) grouping techniques has been implemented, which allows an optimized allocation of computer resources for the node-wise calculation of chemical reactions on the one hand, and the underlying processes such as for groundwater flow or solute transport on the other hand. This technical paper presents the implementation, verification, and parallelization scheme of the coupling interface, and discusses its performance and precision.

1 Introduction

Reactive transport modeling is an important approach to better understand, quantify and predict hydro-biogeochemical processes and their effects on subsurface environments. It is of growing interest among the fields of geotechnical engineering applications and environmental impact assessments and is used e.g. in contaminated site remediation or water resources management, to predict the environmental fate of organic and inorganic substances and pollutants in soil or groundwater reservoirs (e.g. Ballarini et al., 2014; Hammond et al., 2010, 2011, 2014; Henzler et al., 2014; Lichtner et al., 2012; Molins et al., 2010; Riley et al., 2014; Yabusaki et al., 2011). Geotechnical applications employ reactive transport simulations e.g. to quantify geochemical processes in geological nuclear waste repositories (e.g. Kosakowski and Watanabe, ~~2013~~2014; Shao et al., 2009; Xie et al., 2006)

or to evaluate CO_2 geological sequestration (e.g. Beyer et al., 2012; Li et al., 2014; Pau et al., 2010; Xu et al., 2004, 2006).

In the last decades, much effort has been invested to develop practical tools for reactive transport modeling (Steefel et al., 2014), such as PHREEQC (Parkhurst and Appelo, 1999, 2013), OpenGeoSys (OGS) (Kolditz et al., 2012), HYTEC (van der Lee et al., 2003), ORCHESTRA (Meeussen, 2003), TOUGHREACT (Xu and Pruess, 2001; Xu et al., 2006, 2011), eSTOMP (Yabusaki et al., 2011), HYDROGEOCHEM (Yeh and Tripathi, 1990), CrunchFlow (Steefel et al., 2014), MIN3P (Mayer et al., 2002) or PFLOTRAN (Lichtner et al., 2015). Since each code has its own strengths and limitations, the coupling of different codes, i.e. one software ~~applies~~ applied to another and/or vice versa, is ~~an indispensable choice and~~ a straightforward solution to make use of combined capabilities of different codes. Existing approaches, which apply tool coupling methods to simulate reactive transport processes are e.g. HYDRUS and PHREEQC (Jacques and Šimůnek 2005; Šimůnek et al., 2006); COMSOL and PHREEQC (Nardi et al., 2014; Nasir et al., 2014; Wissmeier and Barry, 2011); OGS-GEMs (Kosakowski and Watanabe, ~~2013~~2014; Shao et al., 2009); OGS-BRNS (Centler et al., 2010); OGS-ChemApp (Li et al., 2014); OGS-PHREEQC (Xie et al., 2006; de Lucia et al., 2012); MODFLOW-UFZ and RT3D (Bailey et al., 2013), or MODFLOW-MT3DMS, i.e. PHT3D (Morway et al., 2013).

Due to the complexity of physical, geochemical, and biological processes involved, the development of a reactive transport simulator, which has comprehensive numerical modeling capabilities, is a challenging task. The robustness and computational efficiency of a numerical simulator are of vital importance ~~,~~ because reactive transport modeling is often accompanied with other challenges such as numerical precision and stability (de Dieuleveult and Erhel, 2010; Kosakowski and Watanabe, ~~2013~~2014; Wissmeier and Barry, 2011) or expensive computational time.

Especially for realistic reactive transport simulations at larger scales, i.e. from field ~~scales~~ to catchment or reservoir scale, high complexities of hydrogeological and geochemical systems as well as high spatial–temporal resolution of reactive zones are required to ensure plausible and accurate model results. In these cases, iterative simulations of different sce-

narios or setups e.g. for model calibration and parameter sensitivity analysis becomes extremely difficult and time-consuming on desktop computers with limited computational resources (Hammond et al., 2014; Kollet et al., 2010; Lichtner et al., 2012; Yabusaki et al., 2011).

Parallelization is an established approach to improve computational performance and with the additional benefit from continuous innovation of modern hardware and software development (Hanappe et al., 2011; Wang et al., 2014). PFLOTRAN, a parallel multiscale and multiphysics code for subsurface multiphase flow and reactive transport (Hammond et al., 2012, 2014; Lichtner et al., 2012), or TOUGH-MP, the parallel version of TOUGH2 (Zhang et al., 2008; Hubschwerlen et al., 2012), apply domain decomposition (DDC) methods for their parallel framework. Yabusaki et al. (2011) implemented a one-sided communication and global shared memory programming paradigm in eSTOMP.

A well-designed code concept and efficient parallel implementation can help to reduce the time needed for solution procedures and data communication. Consequently in terms of coupled reactive transport modeling, process simulation and interaction should be closely tied to enable shared data structures and reduce data exchange procedures.

In the current work, OGS has been coupled with the new C++ module of PHREEQC, called IPhreeqc ("I" stands for "interface"). In this operator splitting approach, chemical reactions are calculated locally on each finite element node, whereas processes such as groundwater flow and mass transport are calculated globally. OGS is an open source FEM simulator for multi-dimensional thermo-hydro-mechanical-chemical (THMC) coupled processes in porous and fractured media (Kolditz et al., 2012). In other words, OGS is able to simulate e.g. water and/or gas flow together with heat and mass transport processes in fully and partly saturated media. IPhreeqc on the other hand, inherits all the functionalities of PHREEQC, i.e. it is capable of modelling aqueous, mineral, gas, surface, ion-exchange, solid-solution equilibria and kinetic reactions, but also provides a well-defined set of methods for data transfer and management ~~additionally~~ (Charlton and Parkhurst, 2011). Both codes are open source~~, i.e.~~ ; thus, the technical coupling ~~could~~ can be realized directly on the code level.

The optimum ~~amount~~ amounts of the required computer resources for DDC related processes (flow and mass transport) and chemical reactions can be quite different. In the operator splitting approach, the chemical reaction system is solved on each finite element node individually, so that no node-wise communication is necessary. However, flow and mass transport ~~is~~ are bound to DDC, ~~so~~ meaning that additional communication is needed to exchange the results along shared subdomain boundaries. Therefore a speedup for flow/transport is ~~not given anymore, if~~ no longer experienced when communication and serial fractions are more time-consuming than the parallel fractions. As a consequence, ~~an efficient number of compute cores assigned to the~~ whereas the computation of the chemical system can see a further speedup with the addition of more compute cores, the computation of the transport problem may already reach a ~~maximum limit; while a further speedup for chemical system can still be present with the adding of more compute cores~~ point of optimization, rendering the addition of further compute cores beyond this point inefficient. If the number of compute cores for flow and transport is applied ~~for the attached reactions~~ to the attached reaction system as well, then the most optimal parallel performance cannot always be obtained.

Hence, a new parallelization scheme based on MPI grouping techniques is developed for the OGS#IPhreeqc interface to enable a flexible distribution of different ~~amount~~ amounts of computer resources for DDC related processes and geochemical reactions, thus to allocate optimum number of compute cores for both types of processes simultaneously. Global processes will be parallelized based on the DDC method, whereas the parallelization of geochemical reactions is completely independent from global processes in terms of number of compute cores employed and the way to group finite element nodes for different compute cores.

This technical paper describes ~~in the following the~~ the coupling interface of OGS#IPhreeqc and evaluates the performance of the new parallelization scheme to provide detailed information for modelers and developers to apply reactive transport simulation ~~on~~ to high performance computer infrastructures.

2 Codes and methods

After a brief description of both codes, the coupling interface is introduced and verified on the basis of two benchmark examples. After that, the technical implementation as well as verification of the proposed parallelization scheme is described (Sect. 3).

2.1 OpenGeoSys

Based on object-oriented concepts for numerical solution of coupled processes, OGS provides plenty of possibilities to simulate a broad spectrum of processes related to reactive transport modeling (Kolditz et al., 2012).

For example, OGS can be applied to simulate different ~~kind~~ kinds of flow processes such as incompressible and compressible groundwater flow, overland flow, density-driven flow, unsaturated flow, ~~two phase~~ two-phase as well as multiphase flow. Picard and Newton-Raphson schemes can be applied ~~for~~ to nonlinear problems such as Richards flow and density dependent flow. In OGS, transport of components in fluid phases is simulated based on the advection–dispersion equation. For flow and transport processes, both implicit and explicit time discretization schemes can be used. To couple processes such as flow, transport and heat transport, either the monolithic or staggered approach can be applied (Wang et al., 2011).

Within OGS, geochemical reactions can be modeled by using internal libraries (e.g. the KinReact module for ~~kinetically controlled biogeochemical reactions~~kinetically-controlled biogeochemical reactions; Ballarini et al., 2014) or external couplings with geochemical solvers (e.g. Xie et al., 2006; Shao et al., 2009; Kosakowski and Watanabe, ~~2013~~2014; Centler et al., 2010; Beyer et al., 2012; Li et al., 2014).

OGS has already been parallelized using MPI (Wang et al., 2009; Ballarini et al., 2014) and PETSc (Wang et al., 2014). More detailed information relating to OGS development concept, code resources, benchmarking, etc. can be found at http://www.opengeosys.org/.

2.2 PHREEQC and IPhreeqc

PHREEQC is one of the most ~~widely used~~ widely-used open source geochemical solvers. It provides a variety of geochemical reaction capabilities (Parkhurst and Appelo, 1999, 2013). ~~Beside~~ Besides batch reaction simulations, its current capabilities include inverse and one-dimensional reactive transport modeling. IPhreeqc is a C++ module of PHREEQC which is specially designed for the coupling of PHREEQC with other codes. It provides ~~a well-defined series of methods~~ an application programming interface (API) to interact with a client program (Charlton and Parkhurst, 2011). For example, PHREEQC simulation input data can be prepared as a file or a character string in the client program and executed by PHREEQC with different methods such as *RunFile* or *RunString*. Besides writing selected output results into a file, individual data items at a certain position of the result array can be accessed and returned to the client program by using the *GetSelectedOutputValue* method. More detailed information on IPhreeqc and its data manipulation methods can be found in Charlton and Parkhurst (2011).

2.3 OGS#IPhreeqc interface

In the current study, both source codes, OGS and IPhreeqc are statically linked to allow accesses of all the functionalities of both codes (open source concept). The OGS#IPhreeqc interface is well encapsulated into a general framework for reactive transport modeling in OGS, which has already been described in detail by Beyer et al. (2012). Unlike the previously existing coupling scheme between OGS and PHREEQC presented by Xie et al. (2006), in which the PHREEQC is called externally through a system call to a PHREEQC binary executable, in the new coupling presented here, a call to PHREEQC can be realized directly by accessing functions provided by the IPhreeqc module. The interface itself is version independent and can stay unchanged after updates. For example, the integration of a new IPhreeqc release into the combined code can be realized simply by updating the IPhreeqc source code. Updates which will include/exclude IPhreeqc files

only need a reconfigured list in the ~~CMake file~~build system. This allows users to benefit continuously from code developments of both sides.

The sequential non-iterative (SNIA) approach for operator splitting is applied in the coupling procedure, which means that no iterations are made between mass transport and geochemical reactions. Consequently, adequate small time step sizes are required to reduce the operator splitting errors. Additionally, the Courant-Friedrichs-Lewy (CFL) condition should be taken into account for the spatial and temporal discretization. Figure 1 illustrates the general procedure for reactive transport modeling with OGS#IPhreeqc, which is described in the following.

In the first development step, a file-based approach for data exchange between OGS and IPhreeqc was applied. A character-string based coupling was then developed, which reduces the time consumption for data exchange. The current paper will focus on introducing the character string-based approach. Nevertheless, the parallel performance of both approaches in a cluster will be compared in Sect.4.2.

Within OGS, the model setup is realized by using different input files, which defines specific aspects of the model (e.g. initial-boundary condition). In order to trigger the coupling interface, an additional OGS input file has to be provided, which is very similar to a PHREEQC input file (without the transport module). Based on the file, the interface will define the geochemical system such as reaction types, master solution species etc.

Before entering the time stepping loop, the geochemical system will be initialized first. In order to achieve this, initial values of the system state such as component concentrations and temperatures on each finite element node will be passed to the interface. An IPhreeqc input string will then be prepared, which contains information of the defined geochemical system and relevant values of state variables for all nodes. A call to IPhreeqc will be performed to run the input string. During each time step, after OGS has calculated the flow field by simulating different flow processes mass transport of each mobile chemical component will be calculated. Then same procedures will be performed as during the initialization: concentration values of each component as well as other state variables for all nodes will

be forwarded to the coupling interface; an input string will be prepared, followed by a call to IPhreeqc.

A complete call to IPhreeqc will be realized by taking the following steps: I) create a new instance of IPhreeqc; II) load a thermodynamic database for the geochemical system; III) read and run the specific PHREEQC input string; IV) retrieve the results from IPhreeqc and V) release the IPhreeqc instance from memory. A more detailed description of these procedures and relevant IPhreeqc functions applied can be found in Charlton et al. (2011) and Parkhurst and Appelo (2013).

These procedures have to be repeated during each call to IPhreeqc within each time step. However, the overhead (~~calling of functions~~ steps other than III and IV) involved in the call to IPhreeqc is small compared to the total simulation time, which will be analyzed in Sect 2.4.

After the call to IPhreeqc, the IPhreeqc output string will be handled by the interface during the reaction post-processing. Based on the updated chemical species concentrations, several feedback functions can be applied to update the porosity, permeability, saturation as well as density for flow, heat and mass transport processes. For example, in the case of mineral dissolution or precipitation, the porosity and permeability changes can be evaluated.

2.4 Verification of the coupling interface

The coupling between OGS and IPhreeqc was tested and verified by using several benchmarks for reactive transport problem types such as ion exchange (example 11 of Parkhurst and Appelo, 1999), carbonate mineral precipitation and dissolution (Engesgaard and Kipp, 1992; Beyer et al., 2012), and isotope fractionation (van Breukelen et al., 2005). The latter two benchmarks will be introduced here. A comparison of the computational performance by using different codes will also be presented.

The first presented test example is the Engesgaard benchmark. It ~~describes~~ shows the phenomenon occurs when a 0.5 m long 1-D calcite column is flushed with a solution containing magnesium chloride: calcite dissolves continuously as the solution moves towards

the downstream direction, whereas dolomite precipitates temporarily at the calcite dissolution front. Calcite dissolution/precipitation are simulated as equilibrium reactions, whereas that of ~~the~~ dolomite is modeled as kinetic reactions using a ~~Lasaga-type rate law~~ transition state theory (Lasaga et al., 1994). The kinetic rate parameters from Palandri and Kharaka (2004) are applied (see Table 1). The material properties of the column as well as the initial and boundary conditions are given in Tables 2 and 3, respectively. The model domain is discretized into 100 uniform line elements. Total simulation time is 21333.32 s with a constant time step size of 533.333 s. In the current study, this benchmark is simulated by using OGS#IPhreeqc, OGS-ChemApp and a batch version of PHREEQC (version 3.2.0). A PHREEQC script is provided in Part 1 of the supplementary material. A comparison of the simulation results by using the three codes is illustrated in Fig. 2. Apart from the amount of ~~Dolomite~~dolomite, the simulation results of OGS#IPhreeqc, PHREEQC and OGS-ChemApp (from Beyer et al., 2012) show generally good agreements, as illustrated in Fig. 2. Table 4 lists the execution times by using these codes. For this example, OGS#IPhreeqc is slightly slower than PHREEQC, but around 2 times faster than OGS-ChemApp. Among the total execution time of 7.861 s, the proportion of OGS#IPhreeqc interface ~~and the~~ (including the preparation of input for IPhreeqc and the processing of output from IPhreeqc) and the overhead involved in calling to IPhreeqc (described in Sect.2.3) are 12.7 % and 3.8 %, respectively.

The second benchmark is based on the 1-D multistep isotope fractionation model from van Breukelen et al. (2005), which simulates the sequential reductive dechlorination of tetrachloroethene (PCE) to ethane (ETH) in a 876 m long aquifer over a period of 20 years. The model domain, aquifer properties as well as initial and boundary conditions are illustrated in Fig. 3.

The intermediate products during the degradation include tri- and dichloroethylene (TCE, DCE), vinyl chloride (VC). The whole sequential reductive dechlorination chain is illustrated as follows: PCE $\rightarrow$ TCE $\rightarrow$ DCE $\rightarrow$ VC $\rightarrow$ ETH.

The ^{12}C and ^{13}C isotopes of each chlorinated hydrocarbons (CHCs) are modeled as separate species. ~~Totally~~ In total, there are 11 chemical species including chloride as tracer,

which is produced in each dechlorination reaction. During degradation the kinetic isotope fractionation of each compound is assumed to be constant. More detailed information regarding to the kinetic rate expressions and relevant parameters can be found in van Breukelen et al. (2005). The model domain consists of 120 line elements. The total simulation time is discretized evenly into 100 time steps.

The simulated concentration profile of the light CHC isotopes and relevant $\delta^{13}C$ [‰] isotope signatures along the model domain are compared with those simulated using a batch version of PHREEQC (version 3.2.0) and the KinReact module of OGS (Fig. 4), showing good agreements for both concentration profiles of the light CHC isotopes and corresponding isotope signatures.

Table 5 shows the computational performances by using the three approaches. For this example, the execution time of OGS#IPhreeqc is around twice ~~as much as~~ that of the batch version of PHREEQC. The time spent for the interface and the overhead for calling to IPhreeqc account for 14.7 % and 2.3% of the total simulation time. The KinReact module is much faster than the other two approaches. Nevertheless, it does not have the wide range of geochemical capabilities as PHREEQC does (e.g. surface complexation, mineral nucleation etc.).

3 Parallelization of OGS#IPhreeqc

In this section we describe the parallelization method for the numerical simulation of reactive transport processes with OGS#IPhreeqc. For the parallelization of groundwater flow and mass transport, the OGS internal DDC scheme is employed. For the parallelization of geochemical reactions a loop parallelization is applied. All cores take part in solving the geochemical reaction system, while only certain cores are used to solve the DDC related processes.

3.1 Application of the DDC ~~scheme in~~ approach of OGS

Domain The domain decomposition (DDC) is the procedure to split an initial-boundary value problem (IBVP)into smaller IBVPs on subdomains. In a more figurative sense, the finite element mesh is decomposed into smaller mesh domains.

In the present studyapproach is applied to partition the computational tasks of the global assembly and the linear solver implemented in OGS (Wang et al, 2009). For the current DDC approach, METIS is used as a preprocessing tool for DDC to partition mesh in order to balance the node quantities and minimize the border nodes among subdomains efficiently. Then the information about element indices (global) and the internal border nodes will be extracted and stored in a DDC file. Based on these sub-domains and their mesh topology, the global equation system can be partitioned into local equation systems. For coupled processes different local matrices and vectors are assembled for each process and subdomain in individual CPU cores.

After that the local equation systems will be solved. The local solutions are obtained by a number of product calculations of system matrix and vectors.

Finally, communication is required among subdomains for updating the iteration steps if the components of local With the partitioned mesh data, the stiffness matrix and the right-hand side vector of the system of linear equations are only assembled within subdomains by individual compute cores. Then these assembled subdomain matrices and vectors are associated with border nodes among different subdomains. Furthermore, communication is required as well, when the norm of production from different subdomains needs to be collectedtaken to compute a converged solution with iterative solvers. By this way, the computational tasks of the global assembly and the linear solver are parallelized straightforwardly. More detailed information of decomposition DDC procedures can be found in previous works by Kalbacher et al. (2008) and Wang et al. (2009).

3.2 Parallelization scheme

Figures 5 and 6 illustrate the general idea of the parallelization scheme. The two different MPI groups, i.e. MPI_Group1 and MPI_Group2 and related intra-communicators are created by using MPI functions MPI_Group_incl and MPI_Comm_create. The compute cores

which belong to MPI_Group1 will run most part of the OGS code including all DDC related processes (groundwater flow, mass and heat transport) and geochemical reactions, whereas those of MPI_Group2 will only run a small part of the code related to geochemical simulation.

Technically, this is realized by using the following selection statement, so that the execution of a piece of code can be constrained to processors of the relevant MPI group:

$if(myrank\_group1 != MPI\_UNDEFINED)\{...\}$

For each MPI operation in the entire code, it is important to identify the relevant MPI group and choose the correct MPI communicator.

A "for" loop for MPI_Group2 is created directly in the main function of the OGS code. In each time step, after the calculation of flow and mass transport process, PHREEQC input strings for all compute cores will be created by compute cores of MPI_Group1. A big difference between the serial and parallel algorithm should be noticed here. In a serial simulation, ~~a single~~ only one input string will be prepared for all finite element nodes during each time step (see Sect. 2.3). However, in the parallel simulation introduced here, the information of geochemical system and values of state variables for all the nodes will be distributed into several input strings~~, whose number is equal to that of the total compute cores employed~~. Each string carries the information for the nodes being solved on a specific compute core.

After the preparation of input strings, compute cores of MPI_Group1 will send start signals as well as input strings to relevant compute cores of MPI_Group2, which will invoke the calls to IPhreeqc for compute cores in MPI_Group2 (including all the IPhreeqc tasks described in Sect. 2.3), once the input strings are received. At the same time, compute cores of MPI_Group1 will begin to call to IPhreeqc as well. After PHREEQC calculations are complete in both MPI groups, flow and mass transport processes will start again with the next time step in MPI_Group1, while compute cores of MPI_Group2 will wait for the signal from MPI_Group1 (using blocking receive MPI_Receive) to restart the receiving of input strings and calls to IPhreeqc. After compute cores of MPI_Group1 have run through the complete time stepping loop reaching the end of the simulation, a killing signal will be

sent to MPI_Group2, which will force its compute cores to jump out of the chemical reaction loops. Then MPI_Finalize will be executed to terminate the MPI environment. ~~As a special case~~In special cases, when the number of subdomains equals that of the compute cores, only MPI_Group1 will be created. In this case, no communication between the two MPI groups is required.

As mentioned above, a character string-based data transfer is applied to exchange concentration values between mass transport and geochemical reaction simulations. In each time step, after the simulation of mass transport, concentration values of all components in all finite element nodes will be stored in a global concentration vector. For each compute core a node list vector will be generated through which finite element nodes are allocated to the respective compute core, and their concentration values can be accessed from the global concentration data structure by using this vector. Since the generation of the node list vector is completely independent ~~from~~ of the domain decomposition, flexible groupings of finite element nodes can be realized to ensure an optimum load balance of compute cores for the calculation of geochemical reactions. During the execution of geochemical reactions, each compute core will perform a complete call to IPhreeqc by using a specific input string (including all the IPhreeqc tasks mentioned in Sect. 2.3). A relevant PHREEQC results string will then be generated and sent back to the corresponding compute core of MPI_Group1 (if the compute core belongs to MPI_Group2). After all compute cores finish their calls to IPhreeqc, compute cores of MPI_Group1 will handle all the result strings and store the concentration values of all components in respective local buffers. The values of all local buffers will then be transferred to a global concentration vector by applying the MPI_Allreduce method ~~,~~ (it's a straightforward solution for the current implementation. A more sophisticated approach, however, should be implemented to minimize the inter-processor communication and memory usage), before the updated concentrations of different components are sent back to mass transport process again.

3.3 Computational platforms

The correctness and efficiency of the proposed scheme were tested on two different computational platforms. The first platform is a multi-core Linux machine called "ENVINF". It contains 40 "Intel(R) Xeon(R) CPU E5-2680 v2 @ 2.80 GHz" CPU cores and has a shared memory of approximately 500 GB RAM among these 40 cores. A maximum of 20 cores can be used by a single user at a time. The second platform is a Linux based (CentOS 6 as the operating system) cluster, in the following called "EVE". It consists of 1008 (Intel XEON X5650 @ 2.6 GHz) CPU cores and 5.5 TB of RAM. Computer nodes are connected with 40 GBit s^{-1} QDR Infiniband network interconnect. The peak performance is 10 TFlop s^{-1}.

In order to make the results comparable by using both platforms, for all tests in the EVE cluster, job requests were made to guarantee the use of compute nodes with 20 free slots when submitting to the job queue. ~~Of course jobs~~ Jobs can also be submitted without this constrain, however, since in this case the MPI jobs may be distributed to more compute nodes than necessary in order to allow an earlier execution, more inter-compute node communications may have to be made over the network, which would worsen the performance of the parallelization scheme.

3.4 Verification of the parallelization scheme

The 1-D benchmark of isotope fractionation is extended to 2-D and 3-D to apply the proposed parallelization scheme. Figure 7a and b show the concentration distribution of the light isotope VC along the 2-D model domain and the 3-D model domain at the end of the simulation, respectively. All test results on both parallel computing platforms show very good agreements with serial simulation results.

4 Performance tests and analysis

In this section, the performance of the parallelization scheme is tested by using three examples differing by dimension and problem size. The first two examples are simple extensions

of the 1-D benchmark of isotope fractionation. However, they differ ~~with~~ from each other on problem size. Hence, the influence of the problem size on the parallel performance can be shown. In the third example, geochemical reactions are added upon a saturated-unsaturated flow system. The influence of the simulation of non-linear flow (Richards flow) on the parallel performance can thus be studied.

4.1 Isotope fractionation 2-D

As the first test example, the 1-D PHREEQC model of van Breukelen et al. (2005) is extended to 2-D (876 m $\times$ 100 m, see Fig. 7a). The finite element mesh consists of 1331 nodes and 1200 uniform rectangular elements (120×10). Unlike the 1-D model, here the total simulation time (20 years) is evenly discretized into 200 time steps. With a single core on the ENVINF machine (see Sect. 3.3) the simulation time is 578 s. ~~Chemical~~ The chemical reaction is the most time-consuming part of the simulation due to the simple flow and transport calculations, which takes 92.2 % of the total simulation time.

The performance of the current parallelization scheme is demonstrated in Fig. 8. In Fig. 8a the relative speedup in comparison to a simulation with 4 cores and 4 DDCs is illustrated as a function of number of DDCs and total compute cores. If we fix the number of DDCs at a specific value and vary the total number of compute cores from 4 to 20, we can observe a continuous increase of relative speedup for all DDCs with the growth of the number of compute cores. The speedup of DDC $= 8$ is generally much better than that of DDC $= 4$. Curve AB in Fig. 8a represents relative speedups for combinations in which the number of compute cores equals the number of DDCs. In Fig. 8b curve AB is once again illustrated ("total") together with the relative speedups of IPhreeqc calculation (which includes the complete call to IPhreeqc) and groundwater flow and mass transport. We can observe that the speedup of flow and mass transport reaches its maximum when ~~the number of compute cores exceeds 16.~~ 18 DDCs are applied. As shown by Wang et al. (2009), the adding of subdomains will increase communication between subdomain border nodes. ~~As a consequence~~In this example, the parallel efficiency for ~~calculation of DDC related processes will reduce when number of border nodes becomes comparable with the total~~

~~number of finite element nodes~~solving flow and mass transport degrades already when more than 8 DDCs are employed, for which the border nodes only account for around 6 % of the total nodes. Further increase of the number of DDCs up to 20, yielding 17 % of border nodes, decreases the parallel efficiency down to 0.5 almost linearly. The speedup of reaction~~however~~ , however, is generally much better and increases continuously as more compute cores are provided. In the operator splitting approach chemical reactions are solved locally on each finite element node~~, hence~~; hence, no direct communication among different nodes is necessary.

Figure 8c and d show the breakdown of the total time for different compute cores with a DDC = 4 and a DDC = 12. It is clearly shown that the chemical reaction is the most time-consuming part of the simulation in both cases. With a DDC = 4, reactions take up to 86.5 % of the total time when only 4 compute cores are applied, and drops to 57.2 % if 20 compute cores are applied~~;~~ , whereas for a DDC = 12 it becomes 80.5 % of the total time for 12 compute cores, and goes down to 73.1 % for 20 compute cores. In both cases time for flow and mass transport stays almost unchanged for different number of compute cores because the number of DDCs is fixed. The time for interface mainly includes preparing input strings for IPhreeqc, communication among different compute cores, and handling output strings from IPhreeqc. ~~Averagely~~ On average, this part of time accounts for 5.2 % and 10.8 % of the total simulation time for DDC = 4 and DDC = 12, respectively.

~~Generally, the way of coupling and parallelization is shown to be efficient already for small sized reactive transport problems in a shared memory system such as ENVINF.~~

4.2 Isotope fractionation 3-D

The second test case is a 3-D extension (876 m × 100 m × 10 m, see Fig. 7b) of the 2-D test example which consists of 134 431 nodes and 120 000 hexahedral finite elements (120 × 100 × 10). The simulation time with 2 compute cores with 2 DDCs on ENVINF is 37.5 h.

Similar to the 2-D test example (Sect. 4.1), for the 3-D test case the relative speedup on the EVE cluster is illustrated as a function of number of DDCs and total compute cores in Fig. 9a; Fig. 9b shows a breakdown of curve AB into speedups of flow and mass transport

processes and chemical reactions. If we use the same number of compute cores and DDCs, a nearly linear speedup with the increase of the compute cores can be observed. By using 80 compute cores simulation time can be reduced to around 37 min. As problem size increases, the speedup effects of both DDC related processes as well as chemical reactions become stronger. Similar to the results of the 2-D example, in the 3-D example geochemical reaction shows a much better speedup (superlinear) than flow and mass transport.

However, if we fix the number of DDCs at a specific value and increase the total compute cores further, the resulting speedup is not so significant, especially for ~~lower number of~~ fewer DDCs (see Fig. 9a). This behavior is somewhat different from what we have observed in the 2-D example.

The reason behind this lies mainly in the fact ~~,~~ that the ratio between the time consumption for reactions and mass transport (flow) are different in these two examples. In the 2-D example, the time consumption for calculation of flow and mass transport is rather low ~~comparing~~ compared with that of reactions. In the 3-D example, the time consumption for flow and mass transport is on the similar magnitude as that of reactions (see Fig. 10a and b). For 20 compute cores with 20 DDCs, flow and mass transport together takes 36.2 % of the total time, whereas that of IPhreeqc calculation is 54.3 %. As a consequence, the saving of time in the calculation of reactions alone, which is obtained by increasing compute cores, cannot bring a significant speedup for the entire simulation.

Fig. 10 compares the total time and its breakdowns by using string- and file-based parallelization approaches for this problem. From Fig. 10a and Fig.10b we can see that there are only slight differences between the two approaches on the time spent for flow, mass transport and chemistry. However, when we compare the time for interface in Fig. 10c, we can find that the string-based approach shows ~~big~~ significant advantages over the file-based one, in which the file reading and writing is realized through the general parallel file system (GPFS). By using string-based data exchange, this part of time is small compared to the calculation of mass transport or chemistry. In worst case, it takes 10.2 % of the total time (80 cores with 20 DDCs)~~;~~ , whereas that of the file-based coupling can reach up to 30.9 % (80 cores with 20 DDCs). Generally, it decreases with the increment of DDCs. For a certain

DDC, this portion of time for the file-based coupling increases dramatically with the adding of more compute cores; whereas that of the string-based coupling is much less dependent on the number of compute cores.

Fig. 10d illustrates the total times for different DDCs. For a fixed number of DDCs, the string-based coupling scales much better than the file-based coupling, as it needs much less time for the interface. It is obvious that the best parallel performance for each DDC can be obtained (which is ~~more close~~ closer to the ideal slope) ~~,~~ when the number of compute cores and that of the DDC stay the same. Hence, to achieve a better speedup for a large problem, it is important to reduce the time consumption for flow and mass transport as well by using more DDCs.

4.3 Uranium leaching problem

This test problem is based on the 2-D example of Šimůnek et al. (2012) and Yeh and Tripathi (1991), which simulates uranium leaching at a mill tailing at a hillslope scale (see Fig. 11). The substitution of calcite by gypsum also occurs with the release of acid and sulfate from the tailing. It is worth mentioning that redox reactions are not taken into account in this example. The water flow in both unsaturated and saturated zone is modeled. ~~Totally~~ In total, 35 species and 14 minerals are considered for geochemical reactions. A detailed description of model setup and the simulation results are available in the supplementary material (Part 2).

The 2-D domain consists of 14648 triangle elements with 7522 nodes. ~~A~~ The total simulation time of 1000 days is discretized into 6369 time steps varying from 1×10^{-7} s to 24000 s. The same time discretization is adopted for all parallel simulations introduced below. The wall-clock time for a simulation of this example with 2 cores and 2 DDCs on the ENVINF machine takes around 6.0 h.

Parallel simulations are performed with combinations of compute cores varying from 20 to 60 and DDCs ranging from 2 to 60. Fig. 12 illustrates relative speedups compared to the simulation with 20 cores and 2 DDCs as a function of compute cores and DDCs. ~~Best~~ The best speedups are achieved by using 60 cores and DDCs ranging between 8 ~~to~~ and

16. By using more DDCs, degradation of parallel performance occurs, which is especially obvious when applying 20 DDCs. This phenomenon is mainly caused by the performance degradation of the linear solver for flow and mass transport. Fig. 13a shows the breakdown of the total time corresponding to speedup curve AB in Fig. 12. Major components such as IPhreeqc, linear solver and interface are illustrated. The time for linear solver increases dramatically after 20 DDCs. Over 40 DDCs there is a slight "recovery" of the parallel performance. The reason is that the performance degradation of linear solver becomes slower, while the time consumptions for IPhreeqc, interface and matrix assembly decrease further. Because 20 cores are applied for all the DDCs varying from 2 until 20, time for IPhreeqc stays nearly the same for these DDCs. It is worth mentioning that the time for the interface can become expensive even by using the string-based coupling ~~, when~~ when a limited number of compute cores is responsible for preparing and processing large number of ~~in-~~ input- and output strings (the number of cores is scale larger than that of DDCs). By applying 20 cores with only 2 DDCs, it takes up to 23.4 % of the total time.

Fig. 13b presents the total time for different DDCs as a function of compute cores. Generally, the parallel performance of this example is poor when compared with the two previous examples, since the minimum time consumption for flow and mass transport, which can be achieved by using DDCs between 8 and 16, has already taken a large proportion of the total time (more than 28 %). In this example, the maximum parallel performance is obtained by using more compute cores (i.e 60) than the number of DDCs (i.e. 8 or 12). This shows the advantage of the present parallelization scheme over the conventional DDC approach, which keeps the number of cores the same with that of DDCs.

5 Conclusions and outlook

This technical paper introduced the coupling interface OGS#IPhreeqc and a parallelization scheme developed for the interface. Furthermore, the parallel performance of the scheme was analyzed.

Although OGS already has native chemistry modules and coupling interfaces with other chemical solvers, the OGS#IPhreeqc interface presented in the current study is indispensable, which can greatly benefit from the wide range of geochemical capabilities and customizable database from PHREEQC. Based on a sustainable way of coupling, the continuous code development and updating from two open source communities can be integrated efficiently. A character string-based data exchange between the two codes is developed to reduce the computational overhead of the interface. ~~Particularly~~In particular, it is much more efficient than a file-based coupling for parallel simulations on a cluster, in which file writing and reading is realized through the GPFS. The parallelization scheme is adjustable to different hardware architectures, and suitable for different types of high performance computing (HPC) platforms such as shared-memory machines or clusters.

The parallelization scheme provides more flexibility to arrange ~~compute~~ computational resources for different computational tasks by using the MPI grouping concept. The appropriate setting of DDCs and total compute cores is problem dependent.

If the time consumption for flow and mass transport is in the same magnitude as geochemical reactions, and a continuous speedup can be obtained (with the compute cores that are available) for the calculation of flow and mass transport, then using the conventional DDC approach will be the best choice, as demonstrated in Sect. 4.2. This is especially the case for large problems, in which the time spent for flow and solute transport ~~become~~ becomes more dominant.

If a problem is dominated by geochemical reactions (e.g. for small to ~~middle sized~~ middle-sized problems with complex geochemical ~~system~~systems), then the new approach (creating two MPI groups) can be advantageous, especially when a further increase of the number of DDCs above the optimum will lead to a strong degradation of parallel performance for flow or mass transport. In this case, better speedups may still be obtained by fixing the number of DDCs at the optimum while allocating more compute cores for the second MPI group to accelerate the calculation of chemical reactions.

Even though the time consumption for the interface has been reduced significantly by applying the character string-based coupling, there is still space for improvement to reduce

the time consumption for communication and data transfer between OGS and IPhreeqc. This would be especially important for the approach to be scalable for a large number of compute cores. A more promising way would be to use an "in-memory" coupling, in which the internal data structures of both codes can be accessed from both sides more directly. This could be feasible and sustainably maintainable if a common idea or even a standard for the shared data structures can be developed together by both open-source communities. Another improvement that can be made is to initialize and finalize IPhreeqc only once during the entire simulation, so that the overhead involved in calling IPhreeqc can be minimized.

Blocking communication techniques, like MPI_Barrier were applied to ensure the correct sequence of process coupling. An unbalanced work load distribution for chemical reactions, like in heterogeneous problems with sharp transient reactive fronts or reaction hot spots, could affect the parallel performance as well. Hence, more intelligent ways to ensure efficient load balance still remain ~~as~~ an important task.

In the current study, the available computational ~~resource was~~ resources were limited. It will be part of the future work to test and evaluate the strengths and limitations of this approach on larger high-performance computing machines.

Recently, the SeS Bench (Subsurface Environmental Simulation Benchmarking) benchmarking initiative has started a project to test the parallel performance of different reactive transport modeling tools. In the near future, more complex benchmarks and real-world applications will be tested in the framework of this project to improve the parallel performance of the current scheme and evaluate the suitable range of applications of similar approaches for reactive transport modeling at different scales.

6 Code availability

The source code for the serial version of OGS#IPhreeqc (file-based) was released as an official version of OGS and can be obtained with the following link under an open source license: https://github.com/ufz/ogs5.

Relevant information for OGS compilation can also be found from there. To use the interface, one has to select the option OGS_FEM_IPQC during CMake configuration. The source code of the fully parallel version (string-based) can be provided after the acceptance of the manuscript, and will be part of the following official OGS releases.

Acknowledgements. This work is funded by Helmholtz Centre for Environmental Research (UFZ), Leipzig, Germany. The authors thank the relevant Integrated Project T31 "Catchment Dynamics" of POF3 and its coordinator Maren Göhler. The authors thank Lars Bilke for his technical ~~supports~~ support for the coupling procedure and Ben Langenberg for ~~helps~~ help in running simulations on the EVE cluster.

The service charges for this open-access publication
have been covered by a Research Centre of the
Helmholtz Association.

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Table 1. Parameters for dolomite kinetics (from Palandri and Kharaka (2004)).

Parameter	Value	Unit
A	0.001	m^2/kg
θ	1.0	-
η	1.0	-
E_a (neutral)	52200	J/mol
log(K_{25}) (neutral)	-7.53	$mol/m^2/s$
E_a (acid)	36100	J/mol
$log(K_{25})$ (acid)	-3.19	$mol/m^2/s$
species (acid)	H^+	-
β	0.5	-

Table 2. Material properties of the 1-D calcite column.

Parameter	Value	Unit
Effective porosity	0.32	–
Bulk density	1.80×10^{3}	$\mathrm{kg\,m^{-3}}$
Longitudinal dispersivity	6.70×10^{-2}	m
Flow rate	3.00×10^{-6}	$\mathrm{m\,s^{-1}}$
Temperature	298.15	K

Table 3. Initial and boundary conditions for the Engesgaard benchmark.

Species	Initial conditions	Boundary conditions	Unit
Ca^{2+}	1.23×10^{-1}	1.00×10^{-7}	$mol\,m^{-3}$
Mg^{2+}	1.00×10^{-9}	1.00	$mol\,m^{-3}$
C(4)	1.23×10^{-1}	1.00×10^{-7}	$mol\,m^{-3}$
Cl^{-}	1.00×10^{-9}	2.00	$mol\,m^{-3}$
pH	9.91	7	–
pe	4	4	–
Calcite	5.7412×10^{-2}	–	$mol\,m^{-3}$
Dolomite	0.0	–	$mol\,m^{-3}$

Table 4. An overview of different portions of the simulation time for the Engesgaard benchmark by using different codes (in seconds).

Codes	Flow and Mass transport	Chemistry and interface	Total
OGS#IPhreeqc	0.047	7.814	7.861
Phreeqc	-	-	5.74
OGS-ChemApp	0.183	23.467	23.65

Table 5. An overview of different portions of the simulation time for the van Breukelen benchmark by using different codes (in seconds).

Code	Flow and Mass transport	Chemistry and interface	Total
OGS#IPhreeqc	0.453	32.218	32.671
PHREEQC	-	-	14.196
KinReact	0.453	0.969	1.389

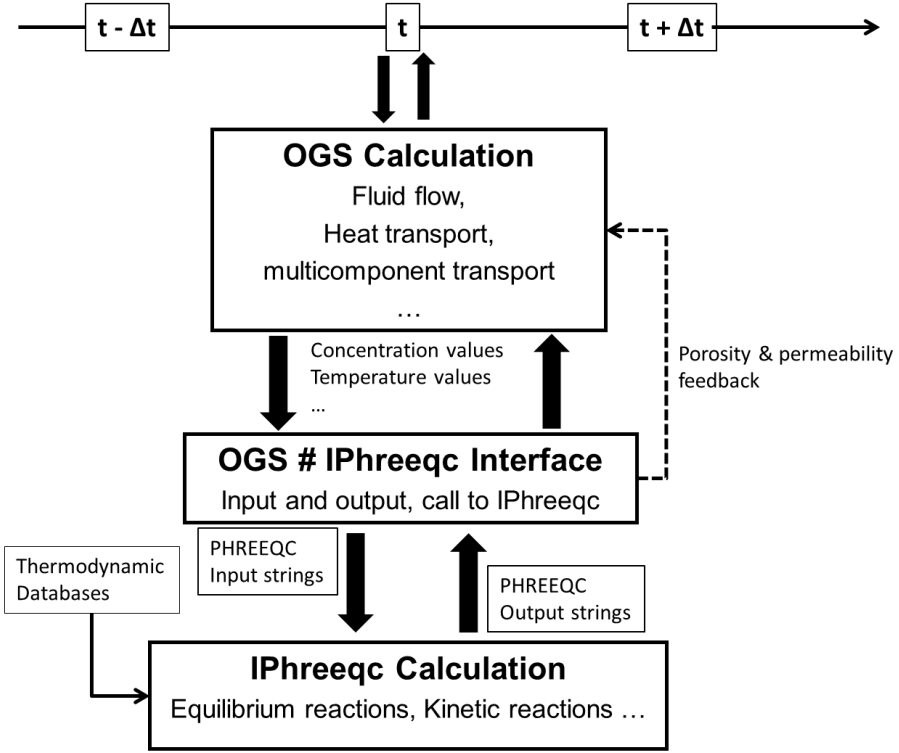

Figure 1. General concept of the coupling interface between OGS and IPhreeqc.

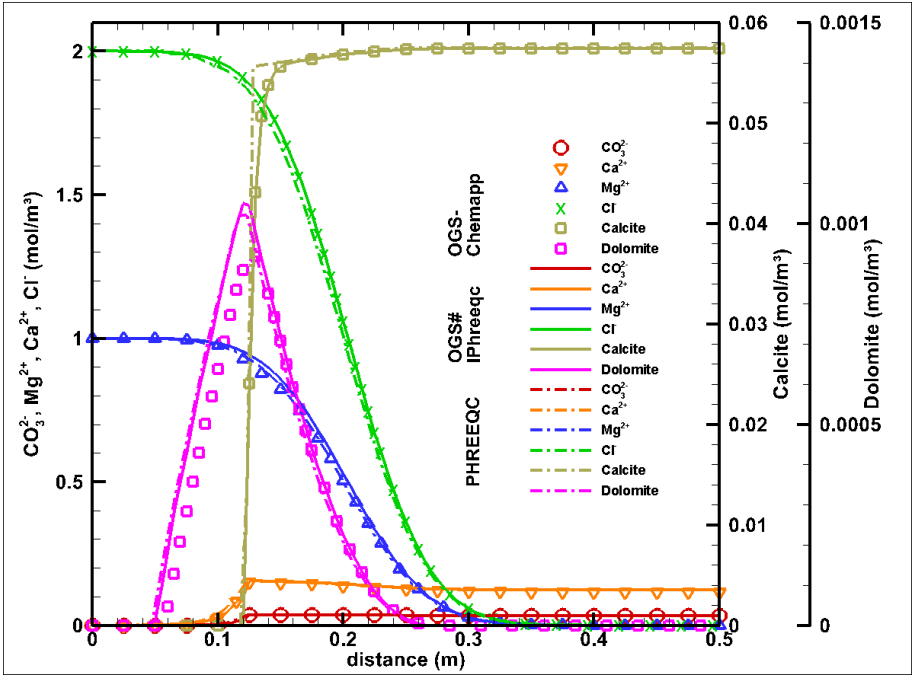

Figure 2. Comparison of calcite and dolomite precipitation/dissolution simulation with OGS-ChemApp, OGS#IPhreeqc and PHREEQC.

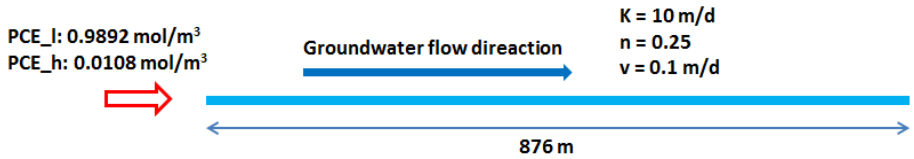

Figure 3. Model domain, material properties, initial and boundary conditions of the isotope fractionation benchmark. K, n and v denotes hydraulic conductivity, porosity and groundwater velocity of the aquifer, respectively (basic units are: m – meter, d – days).

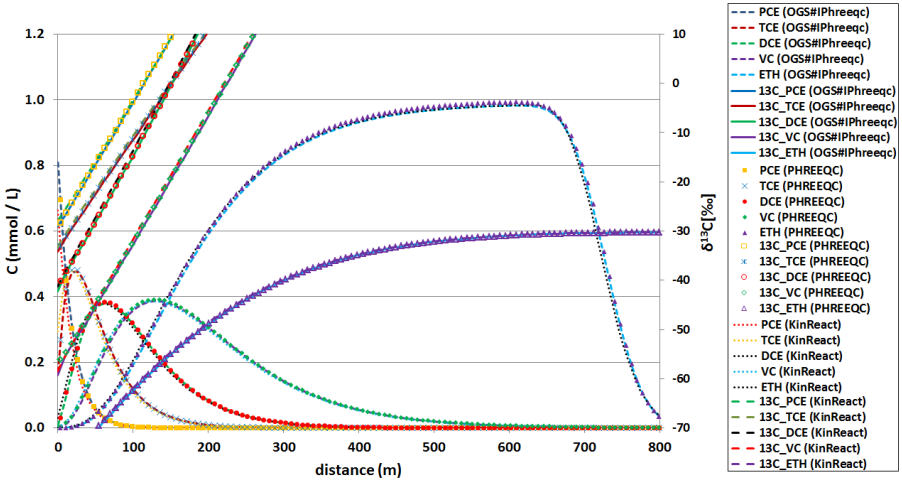

Figure 4. Concentration profiles of the light CHC isotopologues and $\delta^{13}C$ [‰] isotope signatures along the horizontal axis of the model domain simulated by OGS#IPhreeqc (dashed lines or full lines) and PHREEQC (symbols) at the end of the simulations after 20 years.

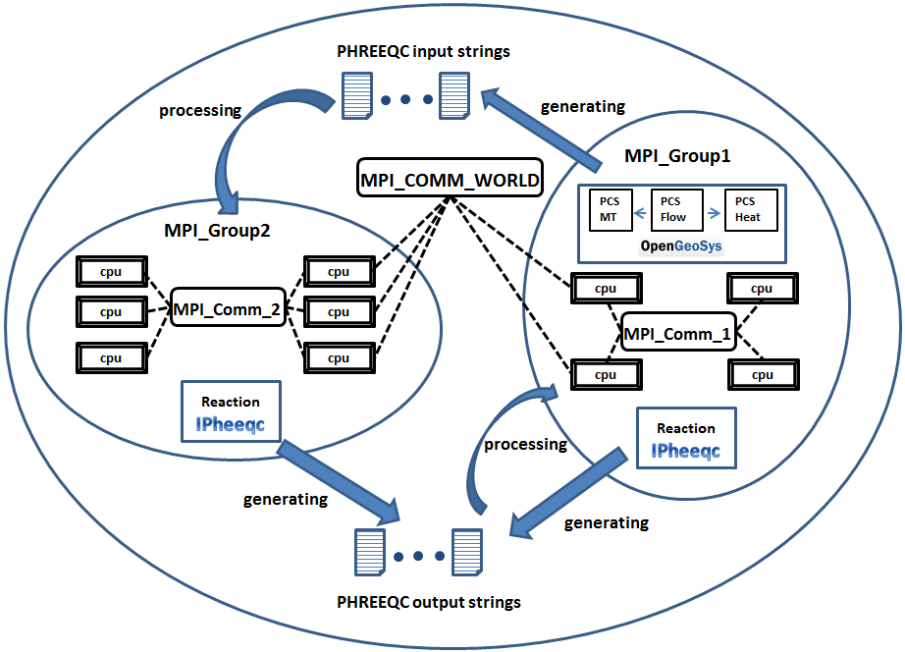

Figure 5. Parallelization scheme for OGS#IPhreeqc. Two distinct MPI groups and relevant inter- and intra-communicators are created. MPI_Group1 take part in the simulation of both DDC related processes and chemical reactions, while MPI_Group2 only participates in the simulation of chemical reactions. PCS MT, PCS Flow and PCS Heat are process of mass transport, flow and heat transport, respectively.

```
if (myrank_group1 != MPI_UNDEFINED)//ranks of MPI_Group1 will run following code
{
    read OGS input data;
    while (the current time is smaller than the end time) //time stepping loop
    {
        compute flow processes;
        compute heat and mass transport process;
        prepare the input strings for PHREEQC;
        send start signal to MPI_Group2;
        //inform MPI_Group2 that the input strings for IPhreeq are prepared;
        send input strings to MPI_Group2;
        calculate chemical reactions with IPhreeqc;
        if MPI_Group2 exists
            receiving result strings from MPI_Group2;
        handle result strings and update data for mass transport;
    }
    print out results; //if needed
    send MPI_Group2 a kill signal;
    //inform MPI_Group2 the time stepping loop is over
    terminate MPI environment;
}

if (myrank_group2 != MPI_UNDEFINED)//if ranks of MPI_Group2 exist
{
    for () //reaction loop
    {
        waiting for signal from MPI_Group1;
        if the signal is a kill signal
            jump out of the reaction loop;
        else
            receive input strings from MPI_Group1;
            calculate chemical reactions with IPhreeqc;
            send result strings to MPI_Group1;
            //inform MPI_Group1 that calculation of reaction is done
    }
    terminate MPI environment;
}
```

Figure 6. Pseudo code for schematic presentation of the parallelization scheme.

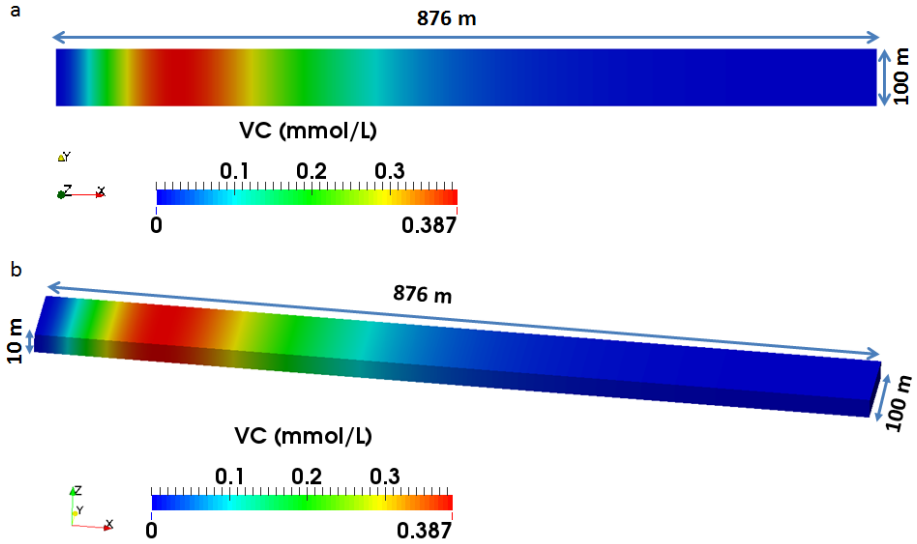

Figure 7. Concentration profile of light isotope VC of the 2-D model **(a)** and the 3-D model **(b)** at the end of the simulation. For **(b)** a vertical (z direction) exaggeration of 2 times is applied.

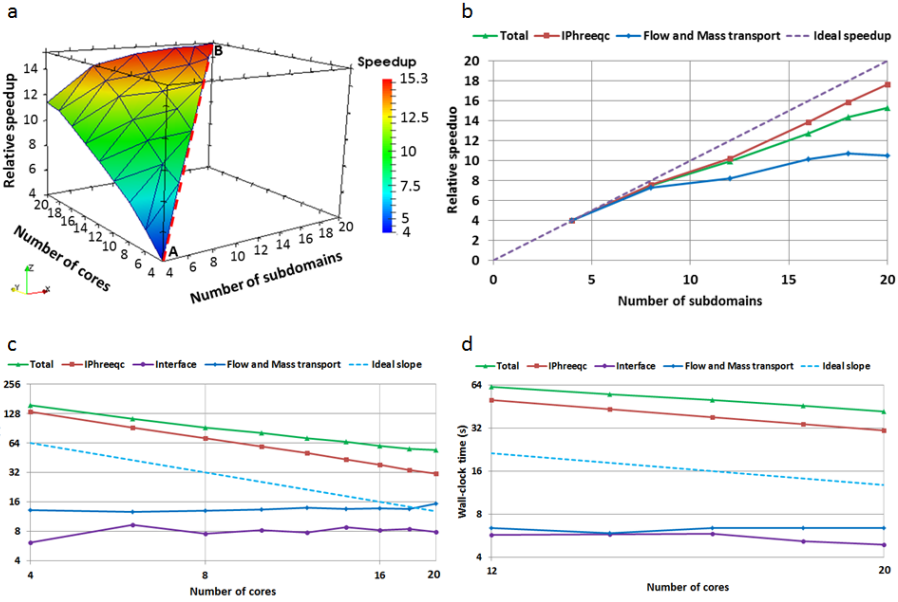

Figure 8. Performance of the proposed parallelization scheme in running isotope fractionation 2-D example on ENVINF. **(a)** Relationship between number of DDCs, number of compute cores and relative speedup in comparison to a simulation with 4 cores and 4 DDCs (Color legend shows the value of relative speedup); **(b)** breakdown of the speedup curve AB (marked as dashed line in **a**) into speedup of calculation of chemical reaction i.e. IPhreeqc and flow and mass transport; **(c)** breakdown of the total time for chemical reactions, interface and flow and transport for DDC $= 4$; **(d)** breakdown of the total time for DDC $= 12$.

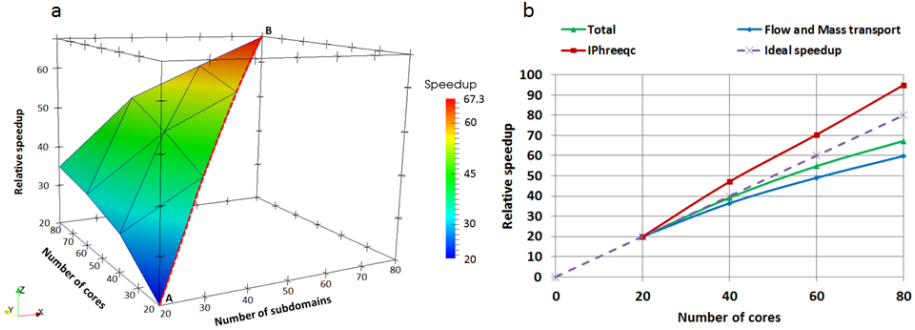

Figure 9. Performance of the parallelization scheme for the simulation of the 3-D test example on EVE cluster. **(a)** Relationship between number of DDCs, number of compute cores and relative speedup to 20 compute cores; **(b)** breakdown of the speedup curve AB (marked as dashed line in **a**) into speedup of calculation of chemical reaction i.e. IPhreeqc and other processes.

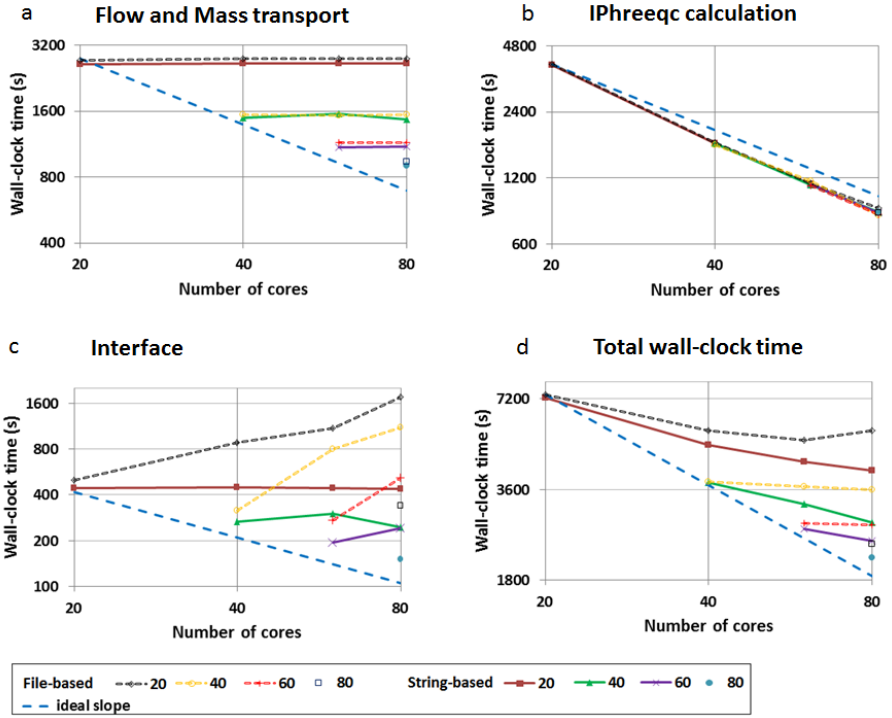

Figure 10. Breakdown of the total wall-clock time in running the 3-D test example on EVE cluster into different processes for different DDCs varying from 20 to 80. **(a)** mass transport and flow; **(b)** geochemical reaction (IPhreeqc); **(c)** OGS#IPhreeqc interface; **(d)** total wall-clock time.

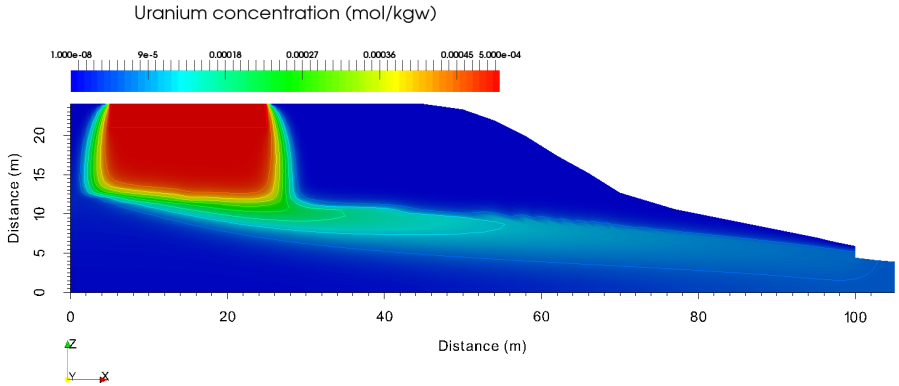

Figure 11. Uranium leaching at a hillslope scale.

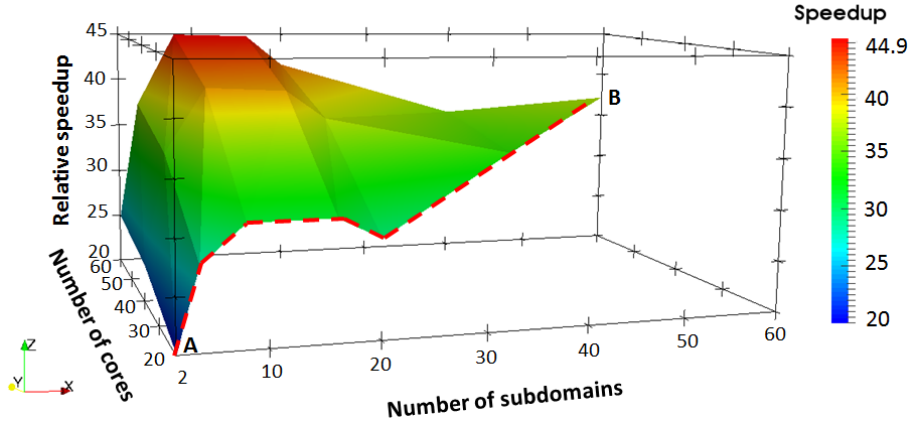

Figure 12. Relative speedup to serial simulation as a function of number of DDCs and compute cores.

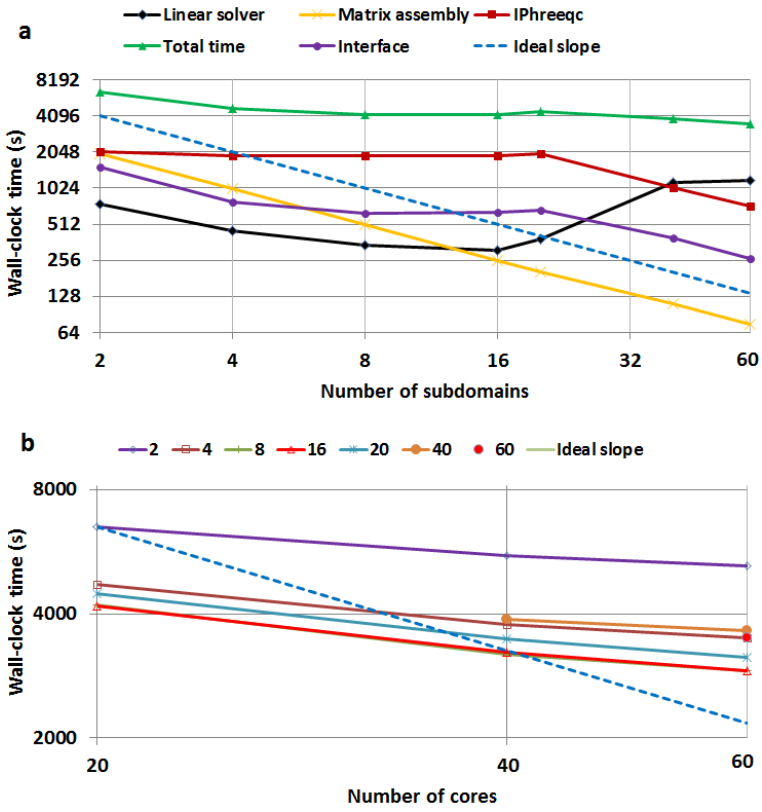

Figure 13. Analysis of the simulation time as functions of subdomains and compute cores. **(a)** breakdown of the total time corresponding to speedup curve AB in Fig. 13. 20 cores are employed for DDCs from 2 to 20, for more DDCs same number of cores and DDCs are applied; **(b)** total simulation time as a function of compute cores for different DDCs varying from 2 to 60.